Layered Materials as High Temperature Membranes in Hydrogen Production

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Outline

- Introduction
- Membrane synthesis
- Membrane characterization
- Transport studies
- Future work

Introduction

- IGCC plants show promise for environmentally-benign power generation. In these plants coal is gasified to synthesis gas, which is then processed in a water gas-shift reactor (WGSR) to produce H_2 for clean-power generation.

- WGSR is a dual-reactor system, the first reactor (HTS) operating at high temperatures, to attain high reaction rates, followed by a second lower-temperature reactor (LTS), which benefits from increased equilibrium conversions at low temperatures.

- The WGSR exit stream contains H_2, CO_2, H_2O and other minor species (e.g., CO). For use in fuel cells (and potentially for CO_2 capture/sequestration), CO_2 is separated using amine absorption or PSA. Both processes are, however, energy- and capital-intensive, and so is the WGSR.

Introduction, cont.

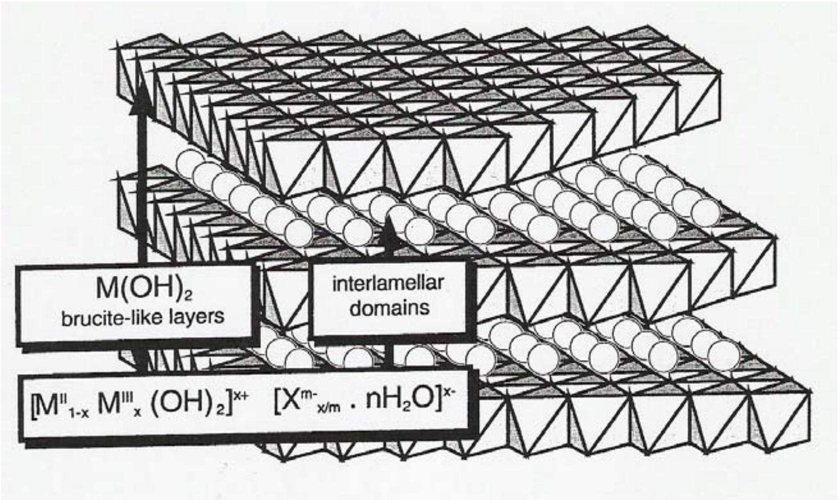
- Our team proposes, instead, a novel membrane reactor (WGSMR), which integrates the WGS and H_2 and/or CO_2 separation steps in a single unit through the use of high temperature membranes.

- The WGSMR has many advantages over the conventional technology. Key to the success of the WGSMR is developing membranes capable of operating in the WGS environment.

What is a Hydrotalcite?

LDH (Layered Double Hydroxide)

$$[M_{1-x}^{(II)} M_x^{(III)} (OH)_2]^{x+} [X_{x/m}^{m-} nH_2O]$$



- $M^{(II)}$:Mg, Mn, Fe, Co, Ni, Cu, Zn,Ga
- $M^{(III)}$:Al, Cr, Mn, Fe, Co, Ni, La
- Anion : m-valence inorganic (CO_3^{2-}, OH^-, NO_3^-), heteropolyacid, organic anion acid

$M^{(III)}/M^{(II)}+M^{(III)}$

$$0.2 \leq x \leq 0.33$$

- Various Applications

  catalysts, catalyst supports, ion exchange materials, adsorbents, medical applications

Membrane Synthesis

- Two different types of membranes have been prepared: Large area membranes and micromembranes.

- For the large area membranes we utilized as supports macroporous hydrotalcite discs, and alumina tubes and discs.

- For the micromembranes we utilized as supports silicon wafers and perforated stainless steel disks.

Membrane Synthesis, cont.

- A number of different techniques have been used for membrane preparation including:
  - Dip-coating using commercial powders and hydrotalcites prepared by our group.
  - Dip-coating using sulfate as a binder
  - Vacuum suction
  - Electrophoretic deposition (EPD)

Hydrotalcites Used in Membrane Preparation

HT material	Mg/Al ratio from ICP-MS	Synthesis Conditions	
		Mg/Al Molar Ratio	Reaction Conditions.
Sasol Mg50	1.29		
Sasol Mg70	3.0		
Sasol Mg70D	3.0	-	4.6% lactic acid added
Sasol Mg70DS[b]	3.0	-	Ball-milled Sasol Mg70
Aldrich HT	2.19	-	-
USC HT 1	2.89	2.9	Stirring 24 h, at 333K
USC HT 2	3.1	3.0	Stirring 24 h, at 333K

Hydrotalcite Synthesis

- We use the co-precipitation method

$Mg(NO_3)_2 \cdot 6H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$

$NaOH + Na_2CO_3$

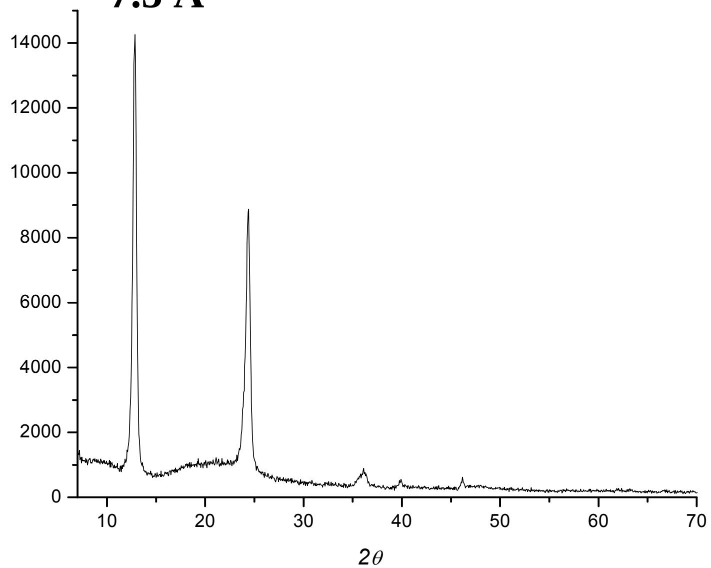
$333\ ^{o}K$, stirring from 2h to 24h

Filtering & Washing & Drying

XRD Spectra

(003)

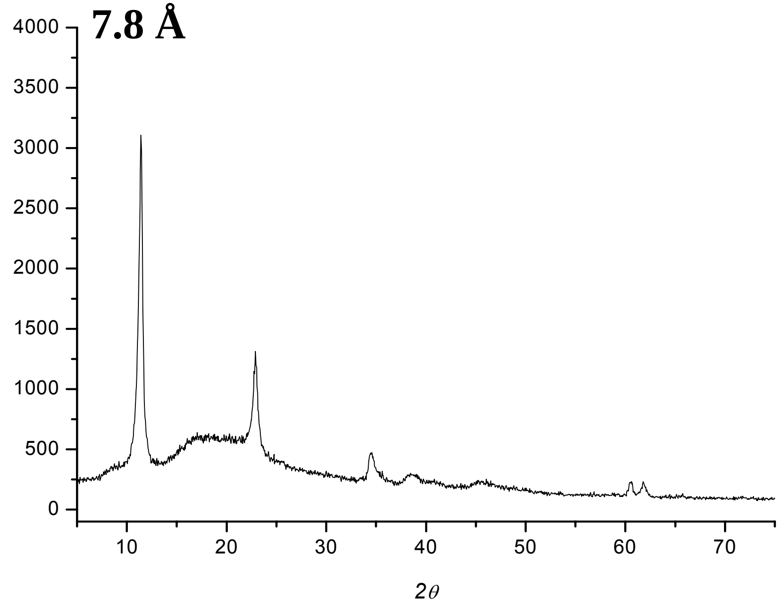
7.5 Å



USC HT

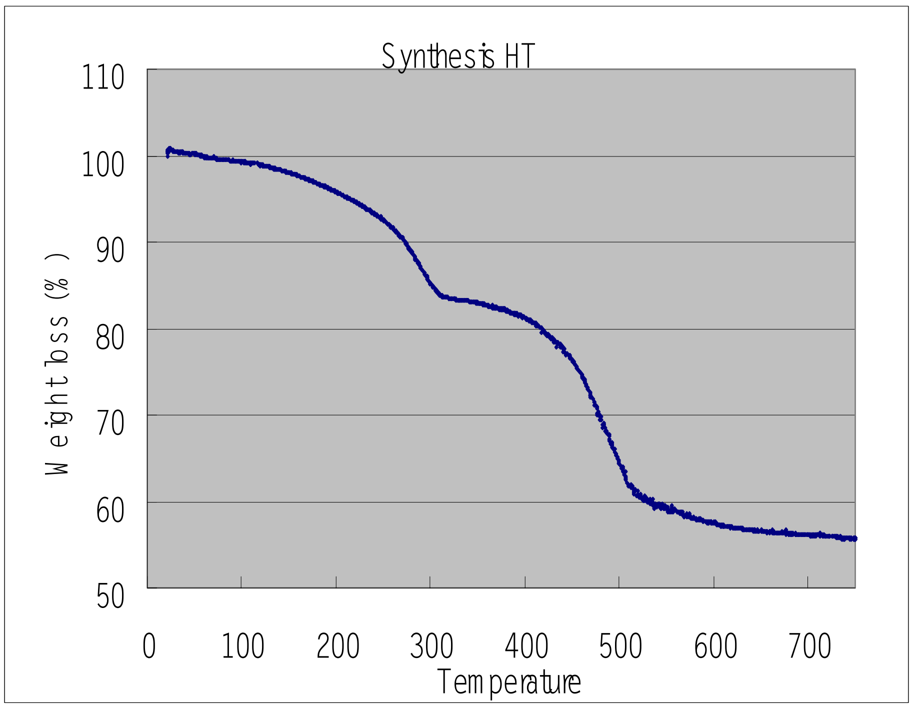
(003)

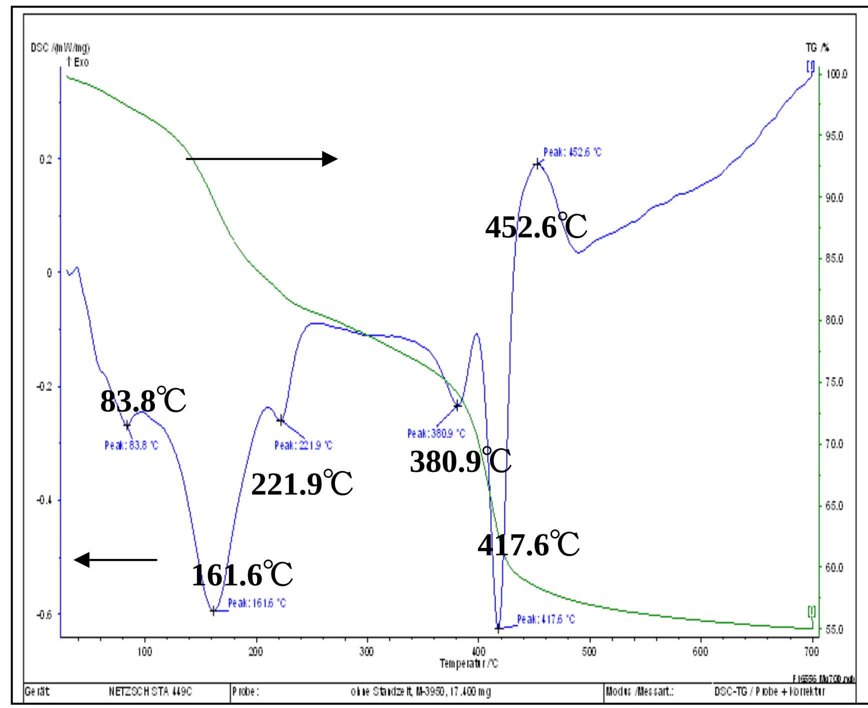
7.8 Å



Mg70D HT

TGA Thermograms



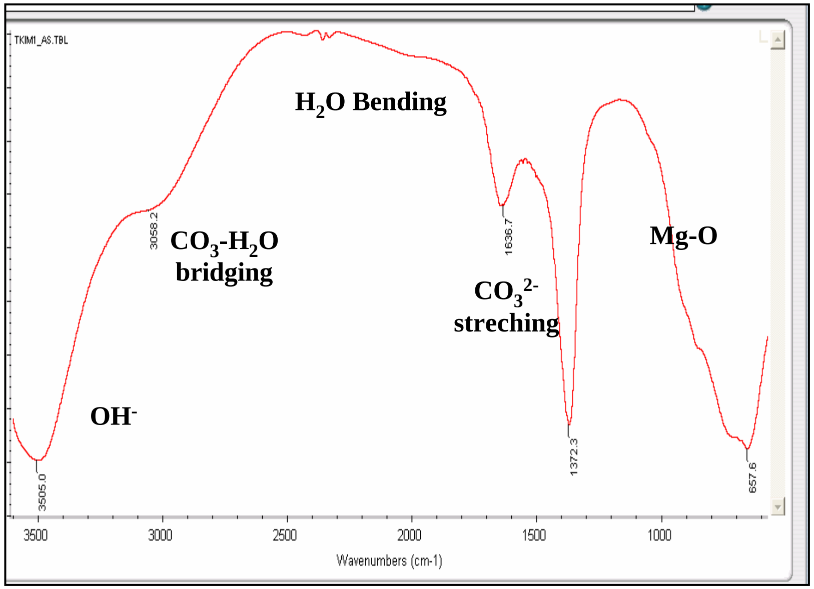


USC HT

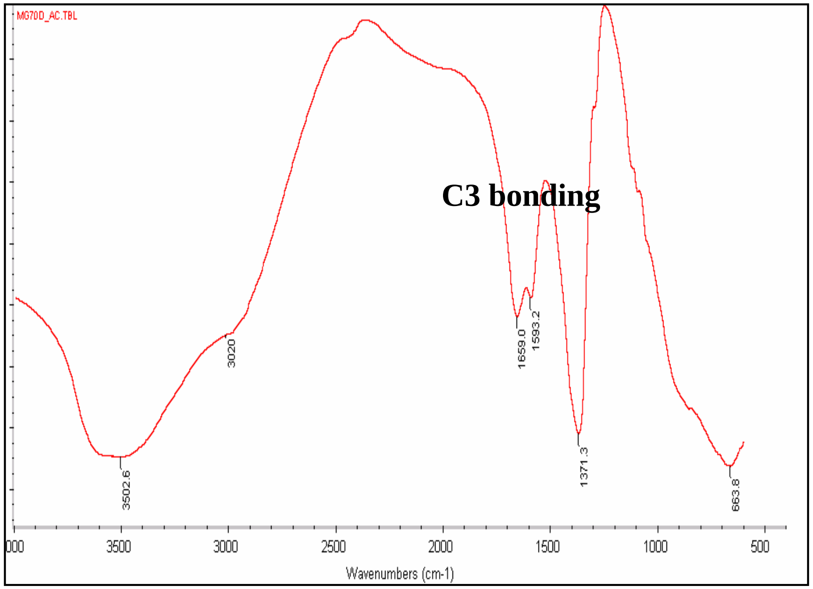
Mg70D HT

FT-IR Spectra

transmission



USC HT



Mg70D HT

Electrophoretic Deposition (EPD)

Electrophoresis is the process whereby colloids travel through a fluid in response to an applied electric field.

$$M = \int_0^t aAc\mu E.dt$$

M=mass deposited in time t

t = deposition time

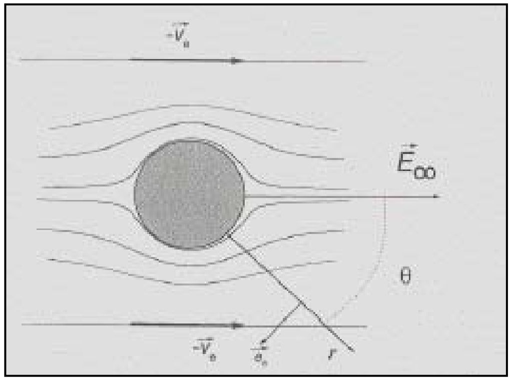
a = co-efficient representing the fraction of particles

A = surface area of the electrode

C = particle concentration in the suspension (kg/m^3)

μ = electrophoretic mobility (m^2/Vs)

E = electric field (V/m)



$$\mu = \frac{ZEV}{4\pi L\eta}$$

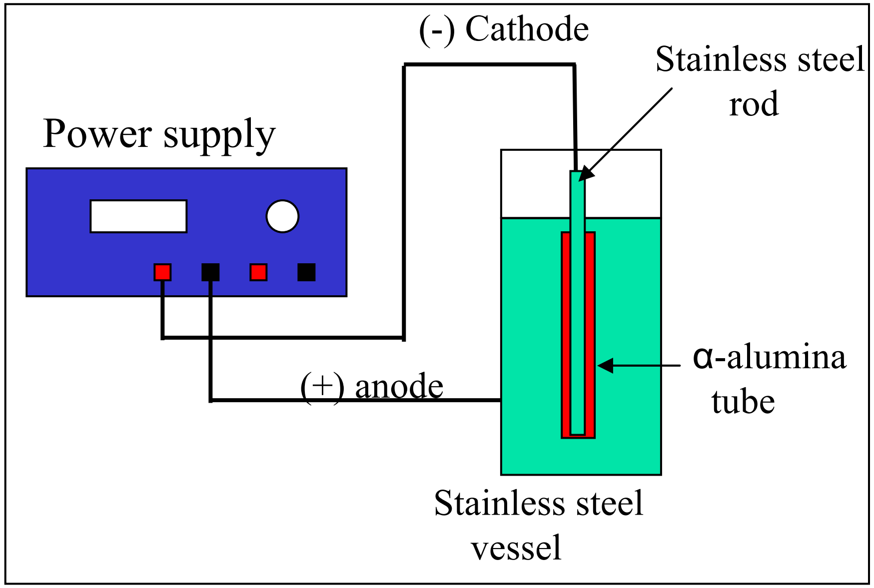
***Z* : zeta potential**, *V* : the applied voltage

E : the dielectric constant of the suspending medium

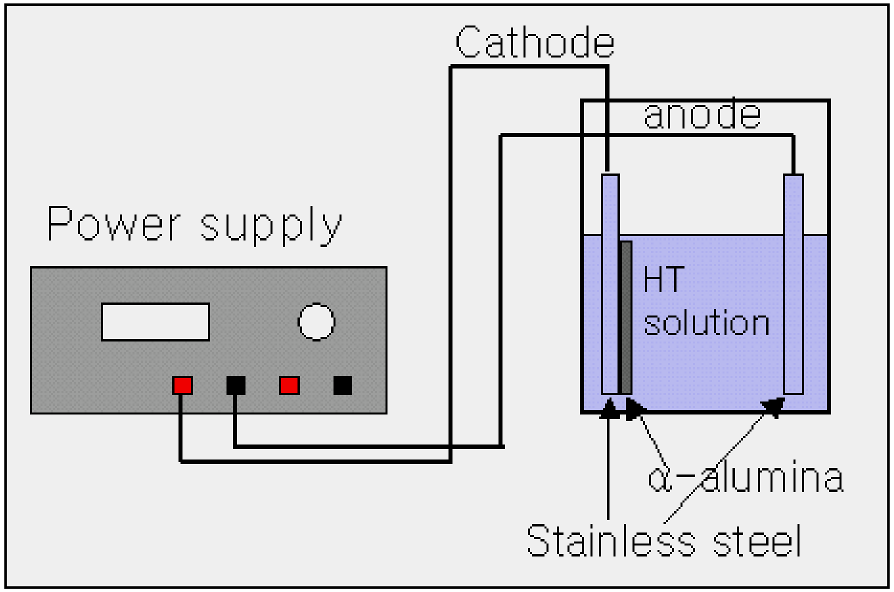
η : the viscosity of the suspension

Schematic of the EPD System

- Deposition parameters: discharge voltage, time, concentration, pH
- Supports: α- alumina (tube, disc), stainless steel porous discs (0.2μm)
- HTc used: Mg 70DS, USC HT



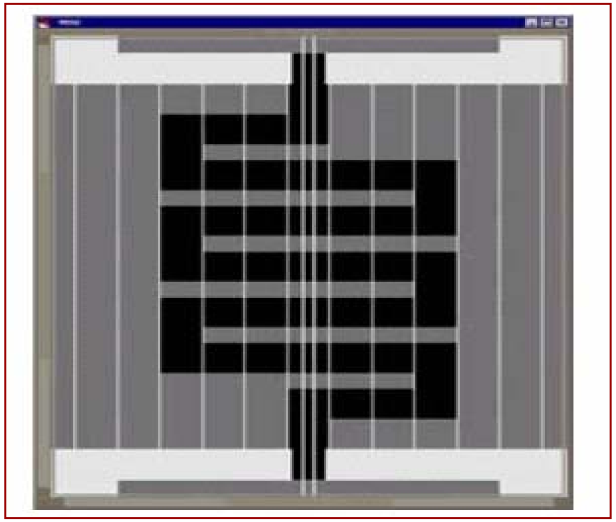
Tube Type



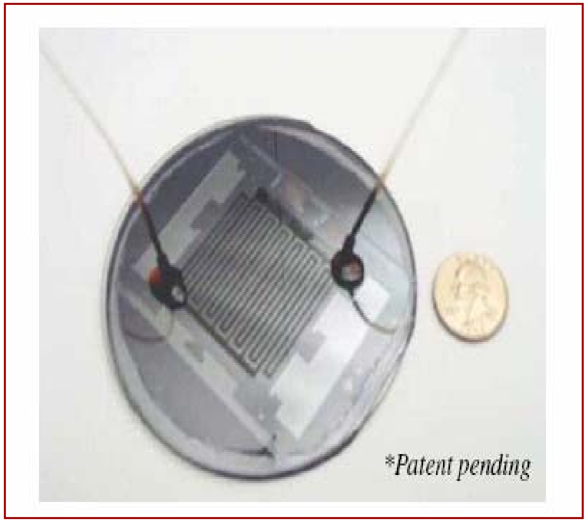
Disc Type

Micromembranes, Why?

- Easier to prepare crack-free for fundamental investigations
- Potential application in micro fuel-cells and microreactors



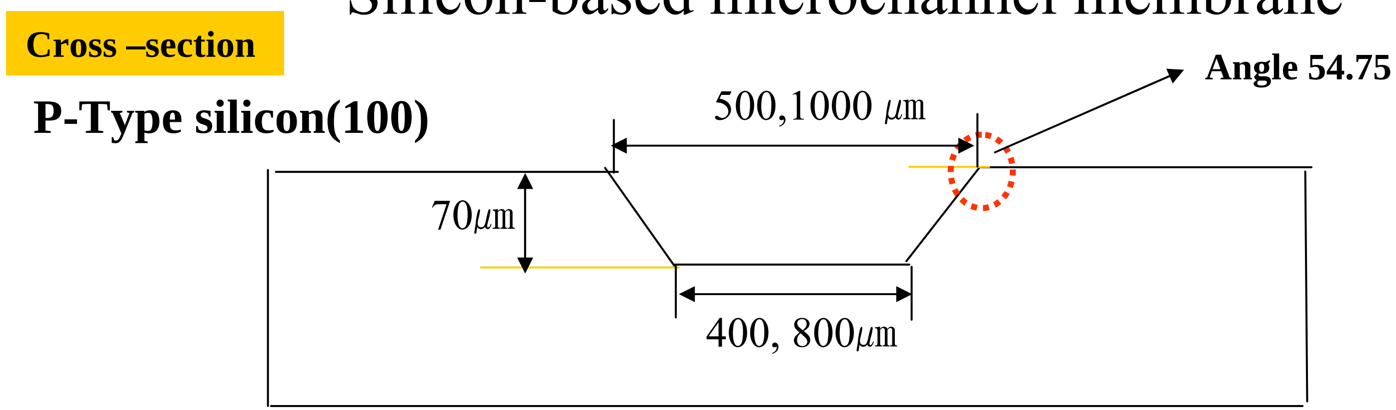
Micro Heat Exchanger

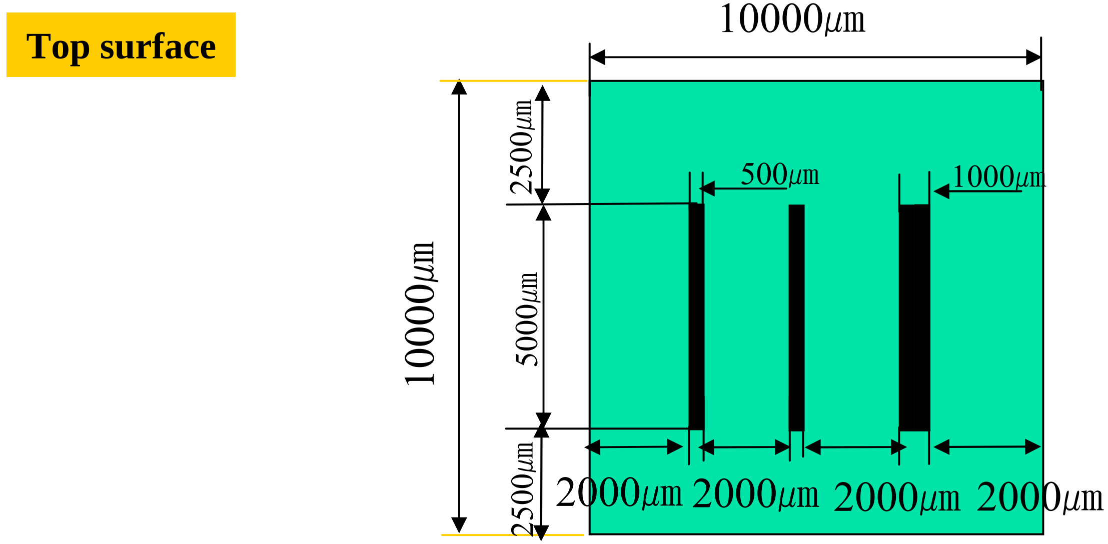


Micro-reactor for Methanol Reforming

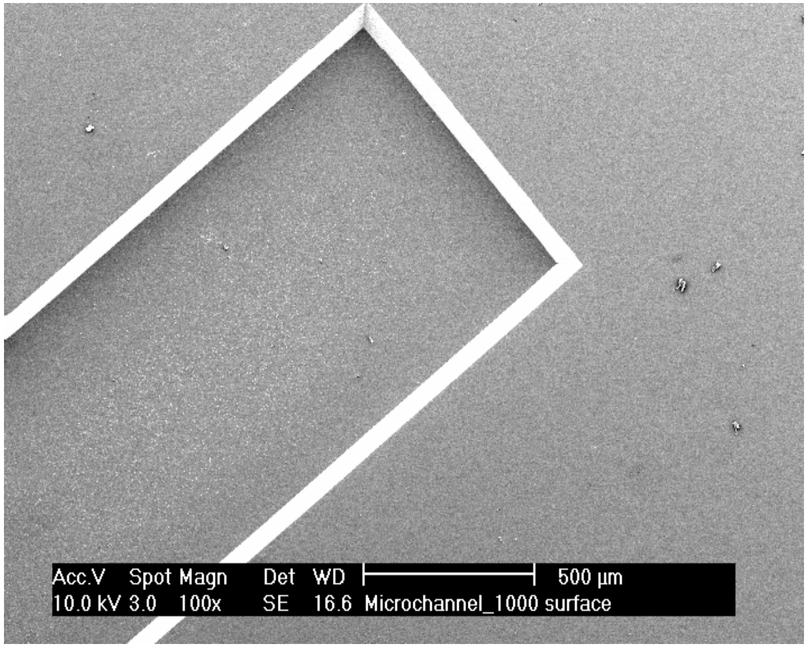
Micromembranes, cont.

Silicon-based microchannel membrane

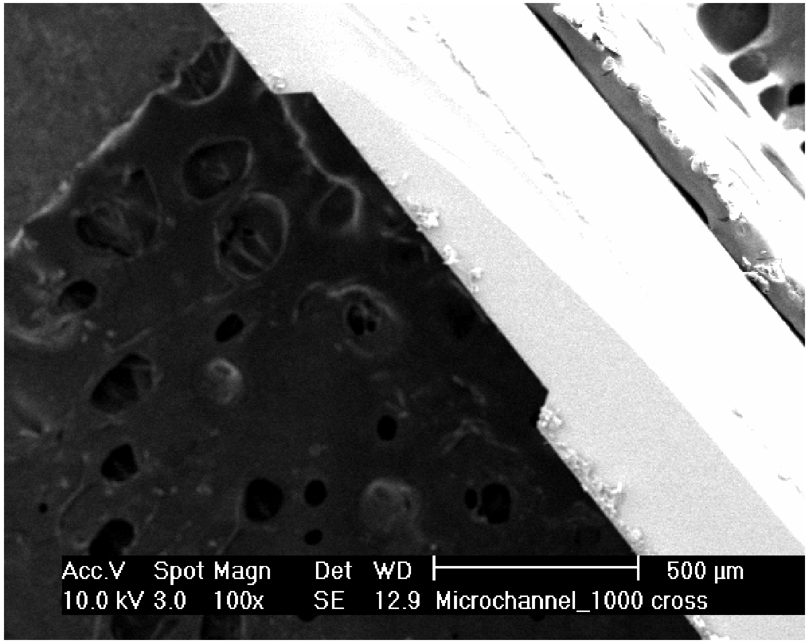




Micromembranes, cont.



Top view (X100)



Cross-section view (X100)

Si-Wafer Supported Micromembranes, Fabrication Process

Photolithography step

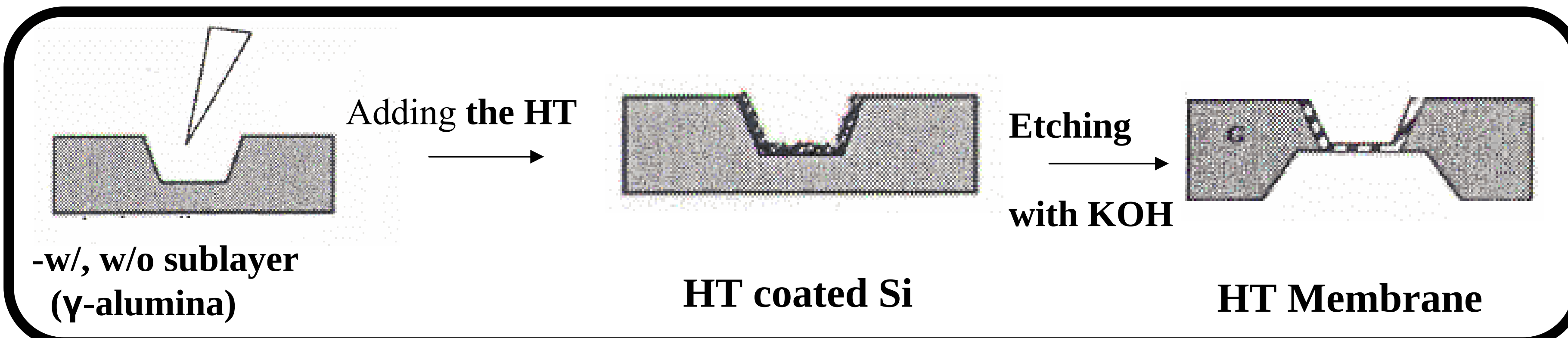
⇩

Etching step

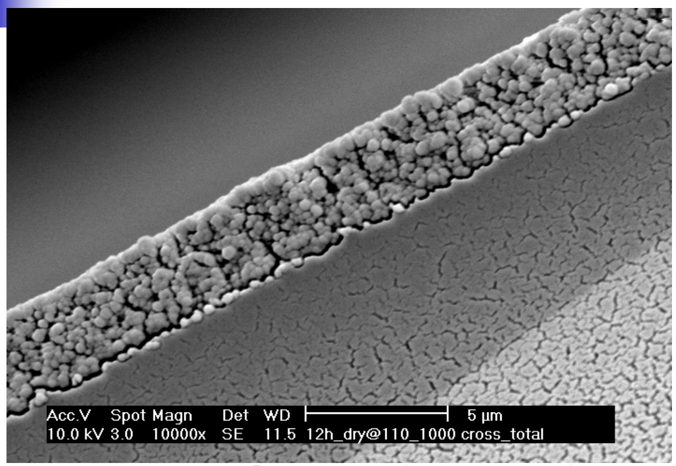
⇩

HT Coating/removing support silicon layer

No	Intermediate layer	Coating method	Conditions
1	None	Colloidal HT coating drop-wise by a micropipette	Dry at 110℃ for 12 h
2		Seed deposition followed by hydrothermal aging	Dry at 110℃ for 12 h (after seed deposition) 160 °C for 24 h (hydrothermal aging)
3	γ-alumina	Colloidal HT coating drop-wise by a micropipette	Dry at 110℃ for 12 h

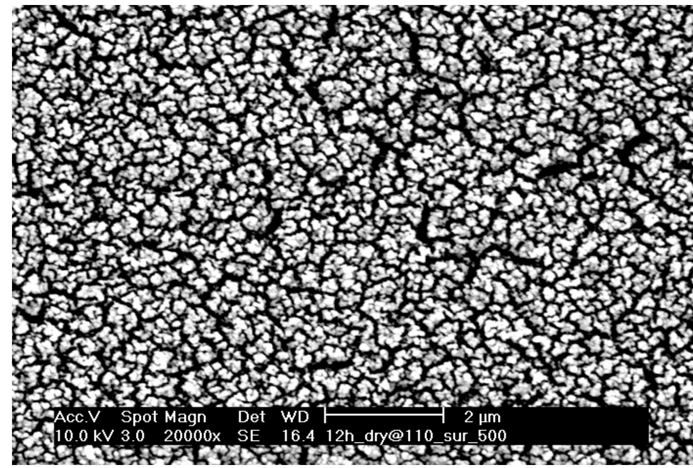


Si Micromembranes, cont.



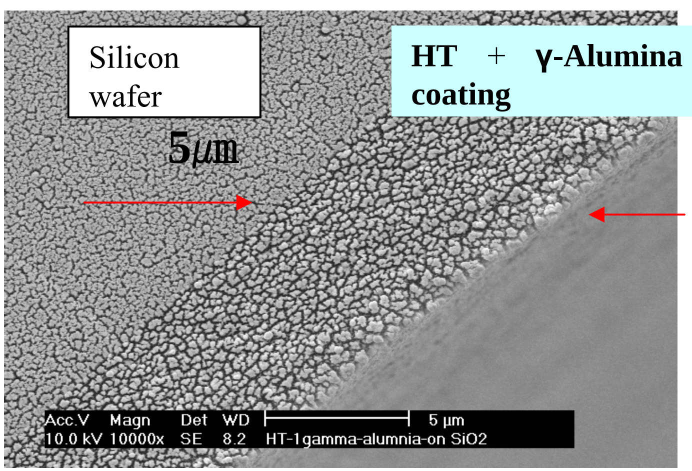
X 1 K

HT membrane on Si, Cross-section



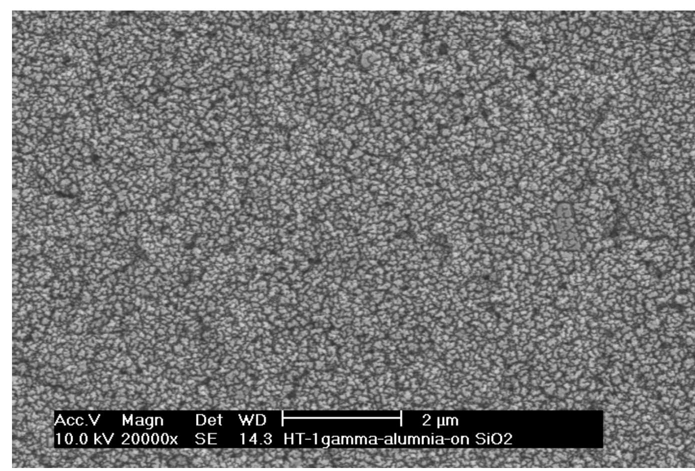
X 2 K

HT membrane on Si, top surface



X 10 K

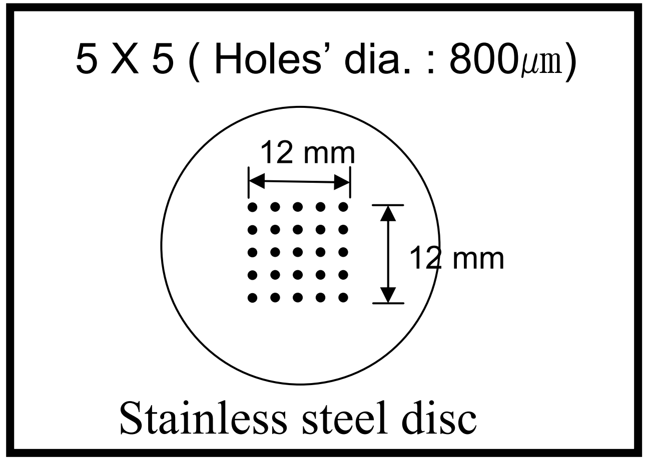
HT membrane on Si with alumina sublayer, Cross-section

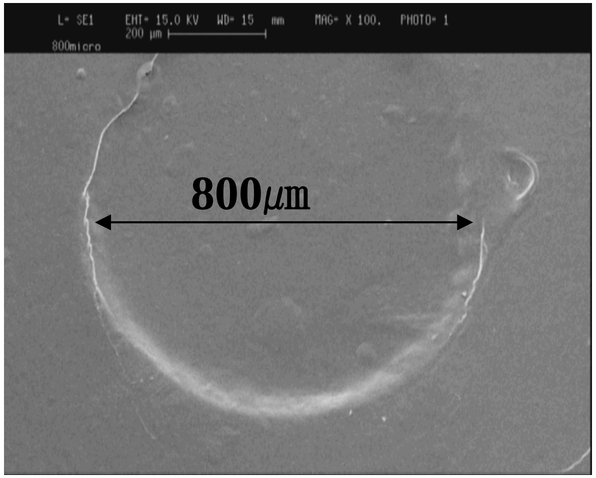


X 20 K

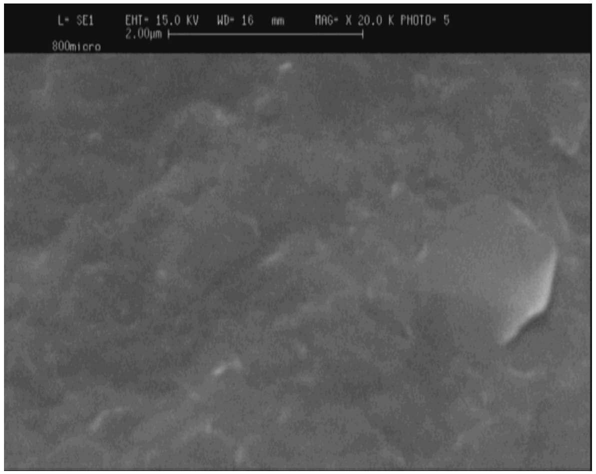
HT membrane on Si with alumina sublayer Surface view)

Stainless Steel Micromembranes



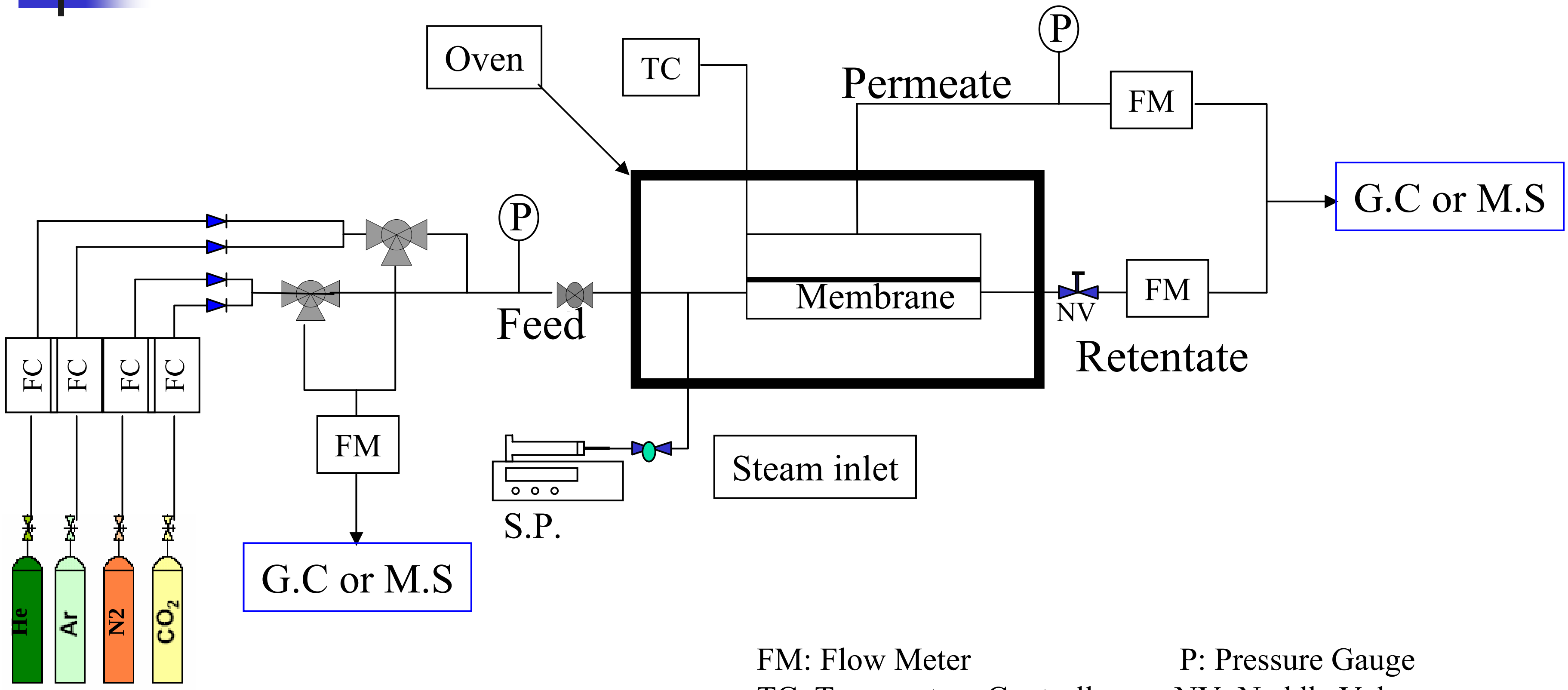


Top surface X100



Top surface X20K

Permeation Apparatus

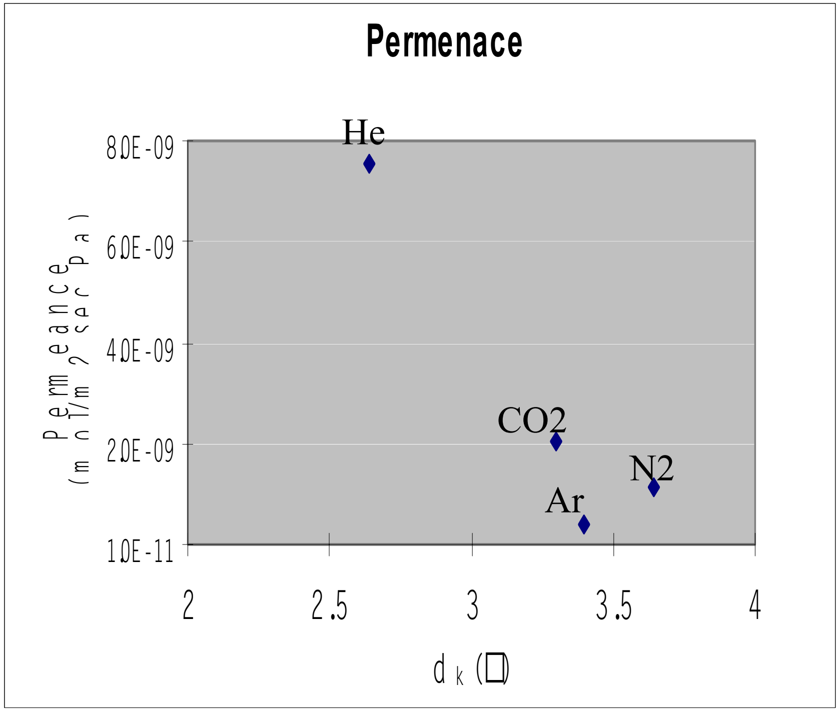


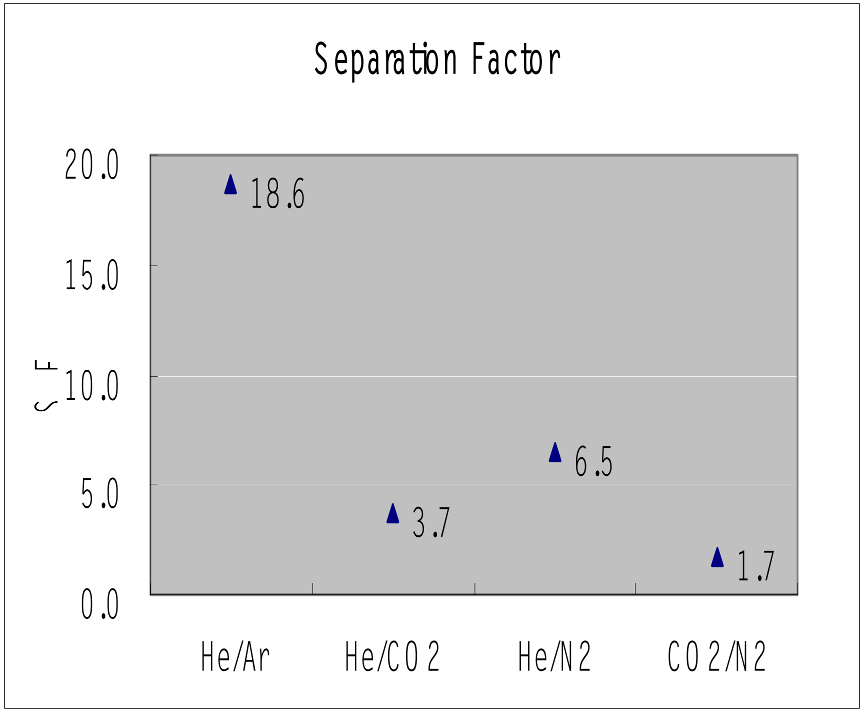
FM: Flow Meter
P: Pressure Gauge
TC: Temperature Controller
NV: Neddle Valve
FC: Flow Controller (Condyne)
SP: Synringe Pump

Micromembranes

$\triangle$**P=30** psi, 25^{o}C

Permenace : N_2 < CO_2





Membranes Prepared with Sulfate Binder

HT source	Coating conditions	Pressure drop (psi)	CO_2	N_2	N_2/CO_2
Mg50	Dip-coating, 3 layers	30	2.65E-08	3.37E-08	1.27
		40	3.11E-08	3.38E-08	1.09
	In-situ 30min	30	1.60E-07	1.46E-07	0.91
		40	1.82E-07	1.65E-07	0.90
	In-situ 3 h	30	3.43E-07	3.07E-07	0.90
		40	3.96E-07	3.56E-07	0.90
Mg70D	Dip-coating, 1 layer	30	1.54E-06	1.72E-06	1.12
	Dip-coating, 3 layers	30	5.63E-07	6.93E-07	1.23

EPD Membranes

Name	Support	EPD conditions				N_2 Permeance (mol/m^2sPa)		N_2/CO_2	
		voltage /coating times	Time	pH	Solution	ΔP		ΔP	
						30 psi	40 psi	30 psi	40 psi
E1	α-Al_2O_3 Tube	1V/1	24 h	12	Synth. HT	1.5×10^{-7}	1.6×10^{-7}	1.16	1.05
E2	γ-Al_2O_3 Tube	2V/4	24h	12	Synth. HT	2.7×10^{-7}	2.9×10^{-7}	1.13	1.17
E3	α-Al_2O_3 disc	2V/3	24h	12	Synth. HT	2.6×10^{-7}	3.0×10^{-7}	1.13	1.03
E4	S-5[a]	1V/1	1 h	7	Mg70DS[b]	2.1×10^{-7}	-	1.28	-
E5	HT disc	1V/1	3h	7	Mg70DS[b]	6.6×10^{-7}	7.0×10^{-7}	1.33	1.29
E6	α-Al_2O_3 Tube	1V/1	1.5h	7	Mg70DS[b]	5.4×10^{-7}	-	0.83	-
E7	S-5[c]	20V/3	1h	7	Mg70DS[b]	2.7×10^{-7}	3.8×10^{-7}	0.75	0.88
E8	S-5[c]	20V/2	1h	7	Mg70DS[b]	2.0×10^{-7}	-	0.86	-

Membranes Prepared by Vacuum Suction

Gas (MW))	Permeance × 10^{-8} (mol/m^2 s Pa)		Permselectivity					
			He/gas			N_2/gas		
	30 psi	40 psi	Ideal Knudsen value	Experimental Result		Ideal Knudsen value	Experimental Result	
				30 psi	40 psi		30 psi	40 psi
He (4)	5.78	5.38	1.0	1.0	1.0	0.38	0.22	0.25
N_2 (28)	1.28	1.36	2.65	4.52	3.96	1.0	1.0	1.0
Ar (40)	0.95	0.96	3.16	6.08	5.60	1.20	1.35	1.42
CO_2 (44)	0.67	0.66	3.32	8.63	8.15	1.25	1.91	2.06

Membranes Prepared by Vacuum Suction, cont

Temp. (°C)	Permeance × 10^{-8} (mol/m^2 s Pa)				Permselectivity				
	He	N_2	Ar	CO_2	He/CO_2	He/Ar	He/N_2	N_2/CO_2	N_2/Ar
25	9.04	1.96	1.49	1.08	8.35	6.09	4.61	1.81	1.32
80	6.62	1.81	0.67	1.10	6.02	9.94	3.66	1.64	2.71
150	4.78	1.08	0.85	0.71	6.78	5.63	4.41	1.54	1.28

Mixed-gas Permeation Tests

Membrane	Number of Coatings	Separation Factor(N_2/CO_2)	
		Single gas	Gas Mixture
Dipcoating [a] by 1.25 wt% Mg70D solution	4	1.3	1.4
Dipcoating [a] by 5wt% Mg70D solution	2	1.27	1.4
EPD E#6 [b]	EPD 1st coating	0.83	0.72

ΔP=30psi, R.T., Feed gas $N_2:CO_2$ = 0.4:0.6,

[a]: α-alumina tube, [b]: Feed gas $N_2:CO_2$ =0.7:0.3

Mixed-gas Permeation Tests

Temp.(K)	Permeance $\times 10^{-7}$ (mol/m^{2}sPa)		Separation Factor (CO_2/N_2)
	CO_2	N_2	
298 K	4.38	3.15	1.39
423 K	4.69	2.86	1.64
473 K	5.05	2.49	2.03

$\triangle P$= 30psi, Feed gas N_2:CO_2=0.7:0.3

Conclusions

- A number of techniques have been developed and studied for the preparation of HT membranes.
- Different membranes have been developed and tested for their permeation characteristics towards single gases and mixtures of gases.
- A number of these membranes were shown to be nanoporous, and some of them show permselectivity towards CO_2.

Acknowledgement

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